I. HYDROGEN PEROXIDE CATALYSIS OF BUTADIENE-STYRENE EMULSION COPOLYMERIZATION

II. BENZOYL PEROXIDE MODIFICATION IN REDOX POLYMERIZATION

BY

CARL JACOB CLAUS

B. S., University of Rochester, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1948

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I. HYDROGEN PEROXIDE CATALYSIS OF BUTADIENE-STYRENE EMULSION COPOLYMERIZATION

Introduction

Because of its cheapness and ready availability, hydrogen peroxide has often been recommended for use as a polymerization catalyst. Early in the government synthetic rubber program it was suggested as a very promising catalyst for rapid butadiene-styrene emulsion copolymerization. The interest in fast polymerization recipes results from the fact that a high polymerization rate permits a lower operating temperature which is known to cause improved polymer properties (1). Hydrogen peroxide in combination with a ferric pyrophosphate complex was early recognized as an effective catalyst system for emulsion copolymerization of butadiene and styrene but it was employed in the form of a complex formula and gave erratic conversions and polymer properties. The mechanism of the initiation process was very little understood.

The primary purpose of this investigation was to develop a simple, rapid polymerization formula involving inexpensive catalyst ingredients, with the hope that it might find practical use in the synthetic rubber industry. Initial exploratory studies made it evident that hydrogen peroxide activated by ferric pyrophosphate offered the best route to a solution of this problem. Another objective was the elucidation of the mechanism of hydrogen peroxide-ferric pyrophosphate catalysis of emulsion polymerization.

Discussion of Results

Hydrogen peroxide with sodium ferripyrophosphate forms a very effective catatlyst system for the emulsion copolymerization of butadiene and styrene. The optimum catalyst

concentrations in the hydrogen peroxide-ferric pyrophosphate recipe are 0.06 g. hydrogen peroxide, $0.02Fe_2(SO_4)_3$ 8.3 H_2O, 0.65 $Na_4P_2O_7 \cdot 10H_2O$, 1.0 soap flakes (Rubber Reserve Standard soap), 40.0 water, 5.0 styrene, 15.0 butadiene. This formula provides an 80 per cent conversion in four hours at 50°.

This polymerization recipe contains no modifier and produces tough, cross-linked, insoluble polymers which break down only with great difficulty on cold milling.

Addition of dodecyl mercaptan to the hydrogen peroxide-ferric pyrophosphate recipe does not affect the rate of polymerization, and produces soluble polymers. The effect of conversion upon benzene-solubility and intrinsic viscosity resembles the relations observed in the mutual recipe.

Most deviations from the optimum system prevent rapid polymerization; a few, however, are of interest and may be of practical importance.

(1) Sodium pyrophosphate peroxide may replace all of the hydrogen peroxide and part of the sodium pyrophosphate in the recipe, with no adverse effect upon polymerization.

(2) Cobaltous salts activate the polymerization reaction, paricularly at temperatures below 50°.

(3) Potassium oleate may replace Rubber Reserve Standard soap but requires readjustment of the system.

(4) This catalyst system may be used to polymerize butadiene, styrene or methyl acrylate in emulsion.

(5) The rate of polymerization is improved slightly by a preliminary catalyst aging technique during charging.

All other variations in the original recipe produced negative results.

Either sodium ferri- or ferropyrophosphate with hydrogen peroxide effectively initiates emulsion copolymerization of butadiene and styrene. Several studies have been made concerning the mechanism by which polymerization is initiated in the hydrogen peroxide-ferric pyrophosphate system. On

the basis of these investigations, the following mechanism is suggested:

The hydrogen peroxide is decomposed completely before polymerization begins. The induction period indicates that it may be converted largely to oxygen, which inhibits polymerization temporarily. Some other constituent of the recipe, probably the soap or the monomer, is oxidized to an organic peroxide, very possibly by a chain reaction initiated by free radicals from the hydrogen peroxide decomposition. This intermediate organic peroxide is then the effective catalyst for polymerization.

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II. BENZOYL PEROXIDE MODIFICATION IN REDOX POLYMERIZATION

Introduction

A method for very rapid copolymerization of butadiene and styrene in emulsion, known as redox polymerization, was discovered by the German chemists during World War II (1). This redox type of activation of polymerization was also discovered independently and nearly concurrently in England (2) and the United States (3). The procedure derives its name from the fact that it employs an oxidizing agent in combination with a reducing agent as the catalyst system. The Germans considered it important to have the oxidizing and reducing agents in separate phases of the emulsion and emphasized the need of a metal of variable valence, preferably an oil-soluble iron compound.

The benzoyl peroxide-ferrous pyrophosphate redox cata-

lyst system, which was adapted from the German recipe recommended by Becker (4), has received much attention in this country. The reason for this interest is the growing knowledge that the lower polymerization temperatures which are made possible by fast recipes of this type cause improvement in the properties of GR-S synthetic rubber (5).

Mechanisms which have been proposed for these redox systems usually postulate an interaction between the oxidizing agent and the reducing agent involving the intermediate production of free radicals due to single electron transfers. Then these free radicals in the presence of monomer are capable of initiating polymerization. In the case of the benzoyl peroxide-ferrous pyrophosphate formula, it is assumed that the free radicals which initiate polymerization arise from the decomposition of the benzoyl peroxide.

This investigation was undertaken in an attempt to clarify the role of the benzoyl peroxide in the benzoyl peroxide-ferrous pyrophosphate catalysis of emulsion polymerization. With this in mind, the influence of catalyst concentration and other polymerization variables upon the molecular weight were studied. Also attempts were made to determine the number and type of end-groups on the polymer chains.

Discussion of Results

The benzoyl peroxide-ferrous pyrophosphate redox recipe, which was developed in these laboratories (6), was employed as the basic formula in most of these studies. It consists of 0.05 g. benzoyl peroxide, 0.1 $FeSO_4 \cdot 7H_2O$, 0.6 $Na_4P_2O_7 \cdot 10H_2O$, 1.0 soap flakes (Rubber Reserve Standard soap), 40.0 water, and 20.0 monomer.

Increasing the concentration of catalyst in the benzoyl peroxide-ferrous pyrophosphate redox system decreases the molecular weight of the polymer. As the concentration of benzoyl peroxide is increased, there is initially a marked decrease in the molecular weight of the polymer but beyond

this, only a slight effect is observed. Simultaneous increase of the benzoyl peroxide, the ferrous sulfate, and the sodium pyrophosphate in the benzoyl peroxide-ferrous pyrophosphate formula reduces the molecular weight to a greater extent than varying the benzoyl peroxide alone. Similar results were obtained in the benzoyl peroxide-fructose system, which consists of 0.1 g. benzoyl peroxide, 0.1 fructose, 1.0 soap flakes (Rubber Reserve Standard soap), 40.0 water, and 20.0 monomer.

The modifying action of benzoyl peroxide was evident at 50°, 30°, and —20°. As expected, a higher polymerization temperature produced lower molecular weight polymer, presumably due to a more rapid decomposition of the peroxide.

The modifying action of benzoyl peroxide on different monomers was also evaluated. Styrene is much more sensitive to catalyst concentration than is methyl methacrylate.

Since the concentration of catalyst is steadily decreasing as the course of polymerization proceeds, any modification due to the catalyst would be expected to decrease. This has been confirmed in the benzoyl peroxide-fructose redox recipe. The molecular weight rises rapidly in the initial stages, but levels off as the reaction proceeds, presumably due to decreased peroxide concentration.

If polymerization in the benzoyl peroxide-ferrous pyrophosphate redox system proceeds by a free radical mechanism, phenyl groups from the benzoyl peroxide should become permanently attached to the polymer. In an attempt to clarify the role of the peroxide catalyst in redox emulsion polymerization, several low molecular weight polystyrenes were prepared in the benzoyl peroxide-ferrous pyrophosphate formula using a large excess of p-bromobenzoyl peroxide. The resulting polymers were analyzed for bromine content. The percentages of bromine which were found corresponded

to an average value of 0.3 or 0.5 of a phenyl group per chain, depending on the method of molecular weight determination.

In the presence of such large amounts of peroxide as were employed in these experiments, the number of phenyl groups attached to the polymer would be expected to exceed one per chain. The initiating reaction should result in the attachment of one phenyl group and any termination due to coupling, reaction with free radicals from the peroxide, or a chain transfer type of reaction with the peroxide should lead to the attachment of another catalyst fragment to the chain. The results of the bromine analyses are much lower than such a concept would predict.

An infrared absorption spectrum of one of these polystyrene samples revealed the presence of benzoate end-groups. There was no indication of an hydroxyl group or a radical from the soap, which might have conceivably become attached to the polymer in the course of the emulsion polymerization.

There was no significant difference between the bromine content of polystyrene prepared at —20° with p-bromobenzoyl peroxide in a redox formula and that prepared at 50°, indicating that temperature has no effect on the number of catalyst fragments occurring in the polymer.

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VITA

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